

Claims

1. (Original) A method for crosslinking one or more molecules, comprising photoactivating a photactivatable crosslinker in the presence of the one or more molecules by one-photon or multi-photon excitation, wherein the crosslinker comprises at least two photoactive groups linked by a bridging moiety, and further wherein the point volume of the activation has at least one dimension of less than about 1 micron; and

crosslinking the one or more molecules with the activated crosslinker.

2. (Original) The method of claim 1, wherein the photoactive groups are selected from the group consisting of benzophenones, monoketals of alpha-diketones or ketoaldehydes, acyloins and their corresponding ethers, benzoin alkyl ethers, 4-aryl-1,3-dioxolanes, triazines, chromophore-substituted halomethyl-s-triazines, pyrazines, pyrimidines, pyradizines, oxadiazoles, chromophore-substituted halomethyl-oxadiazoles, chromophore-substituted disulfides, benzotriazoles, chromophore-substituted azides, phenylglyoxalic esters and derivatives thereof, dimeric phenylglyoxalic esters, peresters, benzophenone tetra-carboxylic peresters, monoacyl phosphine oxides, benzoylephenylphosphine oxides, bisacylphosphine oxides, bis(benzoyl)phosphine oxide, trisacylphosphine oxides, chalcones, cinnamates, nitrobenzenes, phenyldiazenes, pyridazine diones, phthalazine diones, ethyl eosin, eosin Y, fluorescein, 2,2-dimethoxy-2-phenyl acetophenone, 2-methoxy-2-phenylacetophenone, camphorquinone, rose bengal, methylene blue, erythrosin, phloxime, thionine, riboflavin, methylene green, acridine orange, xanthine dye, and thioxanthine dyes, and a combination comprising at least one of the foregoing photoactive groups.

3. (Original) The method of claim 1, wherein the photactivatable crosslinker is substantially water-soluble.

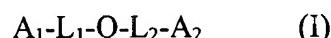
4. (Original) The method of claim 3, wherein the photactivatable crosslinker comprises at least one acid or acid salt.

5. (Original) The method of claim 4, wherein the acid salt is the alkali or alkaline earth metal salt of a carboxylate, formate, nitrate, phosphate, phosphonate, phosphinate, sulfate, sulfonate, or a combination comprising at least one of the foregoing.

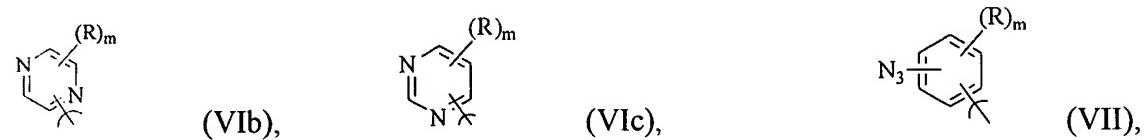
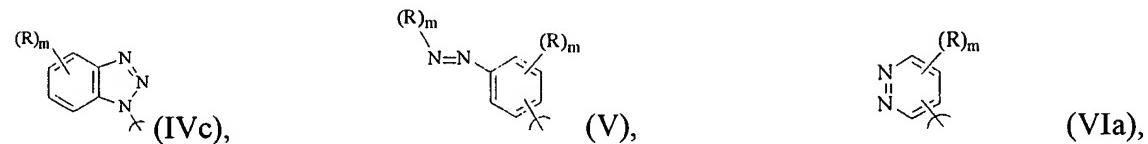
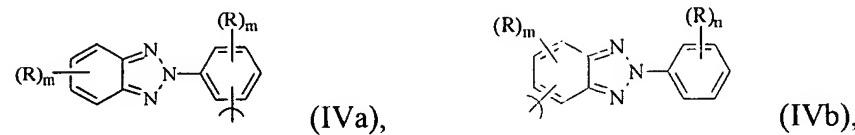
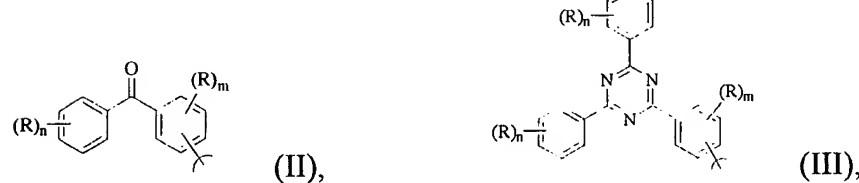
6. (Original) The method of claim 3, wherein the photoactivatable crosslinker comprises at least one base or base salt.

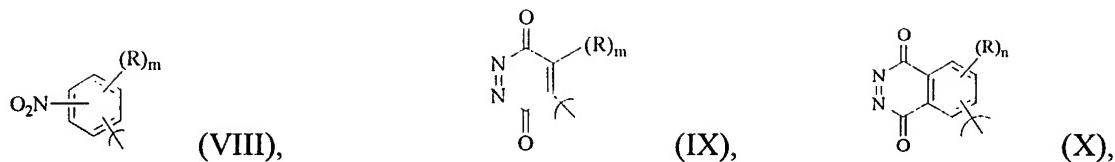
7. (Original) The method of claim 3, wherein the photoactivatable crosslinker comprises at least one group capable of hydrogen bonding with water.

8. (Original) The method of claim 1, wherein the photoactivatable crosslinker has the structure (I)



wherein A_1 and A_2 are the same or different, and are $-(R)_m-N=N-(R)_m-$,





or a mixture comprising at least one of the foregoing structures, wherein

each R in the formulas are independently selected from an ionic moiety; a saturated or unsaturated, substituted or unsubstituted C₁₋₃₆ alkyl, saturated or unsaturated, substituted or unsubstituted C₃₋₃₆ cycloalkyl, substituted or unsubstituted C₆₋₃₆ aryl, or substituted or unsubstituted C₇₋₄₂ alkylaryl; two R groups together may form a fused cyclic or heterocyclic group such as a cycloalkyl or aryl; a halogen, hydroxyl, amino, substituted amino, amide, alkoxy, carboxyl, carboxy ester, phosphate ester, phosphonate ester, sulfate ester, sulfonate ester, sulphydryl group, or hydrocarbonoxy group optionally comprising one of the foregoing hydrocarbon groups

n is 0 to 5 and m is 0 to 4;

L₁ and L₂ are linking groups; and

Q is a bridging moiety.

9. (Original) The method of claim 8, wherein the bridging moiety is a divalent, saturated or unsaturated, substituted or unsubstituted C₁₋₃₆ alkyl, saturated or unsaturated, substituted or unsubstituted C₃₋₃₆ cycloalkyl, saturated or unsaturated, substituted or unsubstituted C₃₋₃₆ methylcycloalkyl, C₆₋₃₆ aryl, C₇₋₄₂ alkylaryl, C₇₋₄₂ aralkyl, C₁₋₁₈ heterocycle, a polyalkylene glycol, polyolefin, polybutadiene, polyisoprene, polyamide, polyester, polysulfone, polyimide, polyamideimide, polysiloxane, polyetherimide, polyether sulfone, polyphenylene sulfide, polyether ketone, polyether ether ketone, polystyrene, polyacrylate, polyacrylonitrile, polyacetal, polycarbonate, polyphenylene ether, polyurethane, polyvinylidene chloride, fluoropolymer, peptide, oligopeptide, oligonucleotide, saccharide, polysaccharide, fatty acid, or lipid.

10. (Original) The method of claim 8, wherein one A₁, A₂, and/or Q comprise an acid or acid salt.

11. (Original) The method of claim 1, wherein the molecule is an amino acid, peptide, oligopeptide, protein, enzyme, myosin, collagen, fatty acid, lipid, ribonucleic acid, deoxyribonucleic acid, oligomer, saccharide, polysaccharide, glycosaminoglycan, cellulose, cytokine, hormone, receptor, growth factor, drug or a mixture comprising at least one of the foregoing molecules.

12. (Withdrawn) A method for the fabrication of a small structure comprising:
irradiating a composition comprising a photactivatable crosslinker and a crosslinkable molecule with one-photon or multi-photon excitation, wherein the crosslinker comprises at least two photoactive groups linked by a bridging moiety; and
forming at least one first portion of the small structure, wherein the point volume of the first portion has dimensions of less than about 1 micron.

13. (Withdrawn) The method of claim 12, wherein the irradiation is with infrared, red, deep red, or visible light illumination.

14. (Original) A product derived by the method of claim 1 or claim 12.

15. (Withdrawn) A photactivatable crosslinker comprising at least two photoactive groups linked by a bridging moiety, wherein the photoactive groups are selected from the group consisting of benzophenones, monoketals of alpha-diketones or ketoaldehydes, acyloins and their corresponding ethers, benzoin alkyl ethers, 4-aryl-1,3-dioxolanes, triazines, chromophore-substituted halomethyl-s-triazines, pyrazines, pyrimidines, pyradazines, oxadiazoles, chromophore-substituted halomethyl-oxadiazoles, chromophore-substituted disulfides, benzotriazoles, chromophore-substituted azides, phenylglyoxalic esters and derivatives thereof, dimeric phenylglyoxalic esters, peresters, benzophenone tetra-carboxylic peresters, monoacyl phosphine oxides, benzoylephenylphosphine oxides, bisacylphosphine oxides, bis(benzoyl)phosphine oxide, trisacylphosphine oxides, chalcones, cinnamates, nitrobenzenes, phenyldiazenes, pyridazine diones, phthalazine diones, ethyl eosin, eosin Y, fluorescein, 2,2-dimethoxy-2-phenyl acetophenone, 2-methoxy-2-phenylacetophenone,

camphorquinone, rose bengal, methylene blue, erythrosin, phloxime, thionine, riboflavin, methylene green, acridine orange, xanthine dye, and thioxanthine dyes, and a combination comprising at least one of the foregoing photoactive groups.

16. (Withdrawn) The crosslinker of claim 15, wherein the photoactivatable crosslinker is substantially water-soluble.

17. (Withdrawn) The crosslinker of claim 15, wherein the photoactivatable crosslinker comprises at least one acid or acid salt.

18. (Withdrawn) The crosslinker of claim 17, wherein the acid salt is the alkali or alkaline earth metal salt of a carboxylate, formate, nitrate, phosphate, phosphonate, sulfate, sulfonate, or a combination comprising at least one of the foregoing.

19. (Withdrawn) The crosslinker of claim 15, wherein the photoactivatable crosslinker comprises at least one base or base salt.

20. (Withdrawn) The crosslinker of claim 15, wherein the photoactivatable crosslinker comprises at least one group capable of hydrogen bonding with water.